CHAPTER II
PREPARATION OF PHOSPHORS AND EXPERIMENTAL ASPECTS
FIG. 1.9. ENERGY BAND DIAGRAM FOR A P–n JUNCTION.

(a) WITHOUT APPLIED FIELD.

(b) FIELD APPLIED IN FORWARD DIRECTION.
2.1 PREPARATION OF PHOSPHORS:

The phosphors are usually prepared by incorporating traces of impurities\textsuperscript{1,2} in a pure semiconductor or insulating crystalline materials. Now a days, phosphors can be obtained in the forms of:

i) Single crystals,
ii) Thin films and,
iii) Microcrystalline powders etc.

2.1.1 PHOSPHORS IN MICROCRYSTALLINE POWDER FORM:

Since in the present study the phosphors being synthesised in powder form the preparation method is described in detail.

A) BASIC INGREDIENTS OF A PHOSPHOR:

The method of obtaining phosphors in powder form, in general, is to start with a pure host material, mix it with a suitable flux alongwith the activator element added as its soluble salt, preferably in the form of solution. The ingredients are then thoroughly mixed and the charge is finally fired at a suitable temperature for a pre-determined period, in a suitable atmosphere.

a) THE HOST MATERIAL:

Since the transitions of electrons responsible for luminescence are within the range of the band gap, for visible luminescence it is
necessary that the band gap of the matrix crystal should be greater than 1.5 eV, the energy of the photon corresponding to the extreme red. For obtaining luminescence in the full visible region it should be greater than 3 eV, the energy corresponding to the extreme violet. Leverenz\textsuperscript{3} prescribed the combination of elements of columns I,II,IIIB, IVA, V, VIA of the periodic table with those of columns VIB and VIIB to satisfy the above condition.

b) **ACTIVATORS** :

Impurities that provide localized energy levels in the forbidden energy gap of an insulator or semiconductor and which permit radiative transitions are called activators\textsuperscript{4}. Depending upon the way of functioning, activators are classified as follows :-

i) **Originator** : It gives rise to new emission lines or bands other than the intrinsic luminescence of the host lattice.

ii) **Intensifier** : It intensifies the intrinsic luminescence of the host lattice.

iii) **Dominant and auxiliary activators** : Sometimes the intensity of singly activated phosphor is enhanced by adding a second activator. The first and the second activators are then known as dominant and auxiliary activators respectively.

iv) **Killer** : It provides energy levels between which radiative transitions are forbidden\textsuperscript{4}. 
v) Co-activator: It provides the balance of charge\(^5,6\) in phosphors activated by monovalent atoms. However, it may also affect the colour of emission, its intensity and the defect structure of the phosphor material.

c) FLUX:

There are certain readily fusible salts which when added to the base material, result in good phosphors\(^7,8\) such salts are known as flux materials or fluxes.

Flux evidently plays different roles in different phosphors. However, it generally:

i) enhances the rate of reaction at relatively lower temperatures\(^9,10\),

ii) promotes the crystal growth at lower temperature,

iii) facilitates the incorporation of activator and its homogeneous distribution in the host lattice\(^9,10\),

iv) affects the luminescence intensity\(^11\), and

v) serves as a charge compensating agent\(^5,6\).

Generally, the effective fluxes are oxysalts, sulphates and chlorides of sodium and potassium\(^12\).

B) PREPARATIVE PARAMETERS OF PHOSPHORS:

The luminescent properties of a phosphor are usually found to depend on a number of parameters during synthesis. Some of the crucial ones are as follows:
a) **PURITY OF INGREDIENTS:**

As luminescence emission is very sensitive to the impurity atoms, a slight trace of any foreign element may cause either activation or poisoning. Hence, the purity of ingredients to be used is an important consideration in making phosphors. A clean laboratory and special attention to maintain purity of ingredients and cleanliness throughout the process are highly essential.

b) **REACTION VESSELS:**

The selection of reaction vessels (crucibles) is to be done on the basis of their chemical inertness, purity, high refractoriness and ability to withstand thermal and mechanical shocks.

c) **FIRING TEMPERATURE AND ITS DURATION:**

To achieve an optimum brightness, the phosphor is required to be fired for a suitable time at an appropriate temperature, empirically determined for each system of phosphor. Also, the temperature within the heating chamber of the furnace must be fairly uniform and constant. Variation in the temperature of the furnace sometimes totally changes the crystal structure of the phosphor and thus affects the structural homogeneity of the final product.

d) **THE ATMOSPHERE OF FIRING:**

The atmosphere in which phosphor ingredients are fired has a pronounced effect on the character of the phosphor. For example, hexagonal CdS, when fired in the neutral atmosphere, emits in the...
infrared region, while it emits in the green region after being heated in \( \text{H}_2\text{S} \) atmosphere\(^{16}\). Also some phosphors\(^{17}\) which do not show electroluminescence response when fired in \( \text{H}_2\text{S} \), become electroluminescent after refiring in the presence of water vapour.

e) **GRAIN SIZE OF INGREDIENTS:**

The grain size of the basic ingredients required for phosphor preparation has a striking effect on the rate of solid-state reaction and thereby upon quality of the phosphor. To have phosphors of good quality, the solid state reaction must be continuous and uniform. This has been achieved when different reacting phases are in intimate contact and therefore, the particles of very fine size with large surface to volume ratio are required.\(^3,18,19\)

f) **RATE OF COOLING:**

In general, rate of cooling affects the luminescent properties such as absorption, spectral emission, the brightness of phosphor and often rate of phosphorescence decay.\(^{20}\) Sudden cooling sometimes even changes the colour of fluorescence.\(^{17}\) Slow cooling rate helps in uniform distribution of imperfections throughout the phosphor.\(^{16}\) On the other hand, rapid cooling preserves the valence state prevalent at high temperature.\(^{21}\)

g) **SIZE OF THE CHARGE:**

Homogeneity of the final product is affected by the size of the charge.\(^{19}\) Preparation of phosphor in large quantities may involve
different rates of heating due to poor conductivity of the charge. The mixture just in contact with the walls of its container will attain furnace temperature earlier than the central portion, forming a temperature gradient within it. The effect may be minimised by taking small quantity of mixture each time.

2.1.2 DETAILS OF PREPARATION OF ZnS:Mn:Cu:Dy(Cl) PHOSPHORS:

Activated phosphors are usually prepared by firing host material along with activators at a pre-determined temperature and a period in a suitable atmosphere. The details of the procedure followed in the present investigation for preparation of ZnS: Mn: Cu:Dy(Cl) phosphors may be divided into two stages. In the first stage, ZnS is prepared by the method of precipitation technique while in the second stage, appropriate quantity of prepared ZnS is fired at pre-determined temperature and period along with the activators.

1) FIRST STAGE:

a) PREPARATION OF ZnS:

ZnS was prepared by using precipitation method. The method followed was based on a process of passing H$_2$S through the solution of ZnSO$_4$ (A.R.) and NH$_4$Cl whose pH was adjusted between 8 and 9. The starting materials such as zinc sulphate, ammonium chloride and ammonia were all of Analar grade purity. The H$_2$S used for precipitation was prepared in Kipp's apparatus using Analar grade chemicals. H$_2$S thus prepared was further purified by passing through various absorbents (air, glass-wool, distilled water, Ba(OH)$_2$ solution etc.).
The precipitate obtained was throughly washed with warm distilled water by vigorous stirring and kept for a day for sedimentation. Washing by sedimentation and decantation was repeatedly carried out till the material was free from chlorides and other soluble impurities. It was then washed with absolute alcohol and finally with distilled water for the complete removal of absolute alcohol. The ZnS obtained was dried in an oven at 70°C. The dry material was crushed, finely ground and sieved. The powder was finally dried in a vacuum desicator.

ii) SECOND STAGE:

a) DETERMINATION OF FIRING TEMPERATURE AND PERIOD:

The optimum conditions of firing were selected in a view of preparing good luminescent phosphors. ZnS along with activators fired at 750°C and above shows both cubic and hexagonal phases upto 1050°C. A temperature higher than this may result ZnS phosphors in a single phase. Phosphors in the present investigation are prepared by firing at 1100°C for 1 hour.

b) PREPARATION OF ZnS: Mn: Cu : Dy : (Cl) PHOSPHORS:

Activators were added in the form of their solutions. The weighed quantities of MnCl₂·4H₂O (A.R.), CuCl₂·2H₂O (A.R.) and dysprosium nitrate (A.R.) were taken and their solutions were separately prepared by dissolving them in double distilled water. The solutions were then diluted subsequently to suit various concentrations of the activators to be added.
A weighed amount of ZnS was mixed thoroughly with requisite amount of activator solutions. The charge was dried in the oven at 70°C and then fired in argon atmosphere for 1 hour at 1100°C. Three different series of ZnS:Mn:Cu: Dy(Cl) phosphors were prepared by varying the concentration of one of the activators and keeping the other two constant. The first series of phosphors contain the fixed amounts of Dy(0.50 wt %) and Mn(0.50 wt %) and varying concentration of copper from 0.00 to 5.00 wt % of ZnS. Similarly, second series of phosphors were prepared by varying the amount of Dy(0.00 to 1.00 wt %) and keeping Cu(0.75 wt %) and Mn (0.5 wt %) constant. The third series was prepared by keeping Cu (0.75 wt %) and Dy(0.5 wt %) fixed and varying the concentrations of Mn from 0.00 to 1.00 wt % of ZnS. Table 2.1 shows the details of the ingredients in the phosphors prepared.

2.2 EXPERIMENTAL ASPECTS:

The details of the experimental techniques followed in studying electroluminescence, thermoluminescence, electro-thermoluminescence, X-ray diffraction, electron paramagnetic resonance (EPR) and scanning electron microscopy (SEM) are as follows:

2.2.1 ELECTROLUMINESCENCE MEASUREMENTS:

The electroluminescence response of the phosphors has been studied with a particular reference to voltage and frequency dependence of brightness and electrical characteristics. The experimental arrangement and the procedure followed are as described below.
A) EXPERIMENTAL SET-UP:

A block diagram of the experimental set-up for the study is shown in Fig. 2.1 while Fig. 2.2 presents a photograph of it. The set-up mainly consists of a source of excitation, an electroluminescent cell and a brightness measuring system.

1) SOURCE OF EXCITATION:

The excitation source used was an audio frequency generator (phillips, type GM 2308/90) with a frequency range of 50 Hz to 16 kHz and having a maximum output voltage of 90 volts. As this voltage was not sufficient to excite the phosphor, a wide band amplifier (Telmax, type sp-100) was used in conjunction with the frequency generator (Fig.2.3). The maximum voltage thus available was up to 2.5 \( V_{\text{rms}} \) in the frequency range of 50 Hz to 5 kHz. At higher frequencies, output voltage dropped significantly and was insufficient to excite the phosphor.

ii) ELECTROLUMINESCENT CELL:

Fig. 2.4(a) shows a schematic view of the EL cell used. The cell consists of a bakelite sheet of size 9 X 5 X 0.7 cms. and a cavity of size 5 X 2.5 X 0.2 cms. grooved in it. In a cavity a conducting glass (resistance 150 ohm cm\(^{-1}\) and transmittance 80%) of appropriate size was fitted. The conducting glass served as one of the electrodes and electrical contact with it was made through a metal plate. Another bakelite sheet, of the same size, was rigidly screwed with the previous one and holds an aluminium plate of appropriate size which
acts as another electrode. The first backelite plate carries a rectangular window of size 2.2 X 1.3 cms. to observe the emitted light. With the cell thus formed, a thin layer of phosphor dispersed in castor oil along with a thin and uniform sheet of mica could be sandwiched between the two electrodes. A thin sheet of mica having high dielectric constant and sufficient breakdown strength excludes the possibility of carrier injection at the electrode contacts.  

The excitation of phosphor could be achieved by applying electric field across the electrodes. The strength of the field was measured using a.c. voltmeter (Ruttonsha Simposon Ac/Dc VTVM 321-I).

iii) BRIGHTNESS MEASURING SYSTEM:

Brightness measuring system consists of a photomultiplier tube, its powder supply and a D.C. nanoammeter. The photomultiplier tube used was "RCA 931 A" having Sb-Cs cathode (cathode sensitivity of 10 \( \mu \) A/lm) and spectral response in the range 3000-7000 \( \nu \) (Fig.2.5). A well stabilized D.C. power supply giving an output upto 900 V was used to operate the photomultiplier tube. To measure output of PM tube a D.C. nanoammeter (NM-122) was used.

B) EXPERIMENTAL PROCEDURE:

i) PREPARATION OF AN EL CELL:

A thin layer of phosphor (125 \( \pm \) 10\( \mu \)) was spread on the aluminium electrode using castor oil (phosphor gives better luminescence with castor oil as dielectric material). The constancy in layer thickness was maintained by taking a fixed volume of phosphor and spreading it over a fixed area. To guard the
against electrical breakdown a thin sheet of mica (thickness $(50 \pm 10) \mu$) was placed over the phosphor layer. The conducting glass was then mounted over the mica sheet. A screw arrangement helped in adjusting interelectrode distance and pressure.

ii) **VOLTAGE AND FREQUENCY DEPENDENCE OF EL BRIGHTNESS**:

The prepared cell was mounted on a platform and below it was placed a P.M. tube. The output of PM tube was connected to D.C. nanoammeter (NM-122). The phosphor was then excited by applying voltage from the exciting source and brightness variations with voltage and frequency were noted. The observations were carried out first by varying the voltage from 0 to $1.5 \text{kV}_{\text{rms}}$ and keeping frequency constant and later by varying the frequency from 50 Hz to 1.9 kHz and maintaining the voltage constant.

iii) **ELECTRICAL CHARACTERISTICS OF PHOSPHORS**:

The simultaneous measurements of brightness, voltage and current were made at various frequencies using the above mentioned set-up. Voltage was measured by using Simpson Ac/DC VTVM 321-I and current by using Philips Polymajor Type PK 5210.

**2.2.2 ELECTRO-THERMOLUMINESCENCE MEASUREMENTS**:

The electro-thermoluminescence (EL-TL) measurements of the phosphors are nothing but thermoluminescence measurements under the action of an applied sinusoidal voltage.

A) **EXPERIMENTAL SET-UP**:

The experimental set-up used essentially consists of (a) source
of excitation (b) suitable EL-TL cell, and (c) the intensity measuring unit.

a) SOURCE OF EXCITATION:

Set-up consisting of an audio frequency generator in conjunction with a wide band amplifier, as already described in sec 2.2.1-A under electroluminescence measurements, was used as a source of excitation.

b) ELECTRO-THERMOLUMINESCENT CELL:

Suitable EL-TL cell, fabricated in the laboratory, consists of an usual condenser type EL cell (as described in sec 2.2.1-A) provided with an arrangement for heating the sample at an uniform heating rate. The schematic view of EL-TL cell is illustrated in Fig. 2.4(b). The system was capable of raising the temperature of phosphor at a convenient heating rate. At lower heating rates the derivative of the temperature versus time curve was constant to within 2%, while at higher rates this increased to 5%.

c) INTENSITY MEASURING UNIT:

It is the same unit as that used in electroluminescence measurements.

Fig. 2.6 shows a block diagram of the complete set-up used in EL-TL measurements.

B) EXPERIMENTAL PROCEDURE:

A thin layer of phosphor embedded in a castor oil was spread on a brass plate and was covered with a mica sheet. A conducting glass placed over the mica sheet served the purpose of one electrode,
while the brass plate acts as other electrode. The EL-TL cell thus prepared was mounted on a platform. The photomultiplier tube was positioned so as to receive the emission from the cell. The cell was energised by an a.c. voltage derived from an audio frequency generator in conjunction with a wide band amplifier, and simultaneously heated with a constant heating rate. The intensity was measured as a function of temperature using d.c. nanoammeter (NM-122). The measurements were carried out by varying one of the parameters, i.e. either voltage or frequency or heating rate keeping other two constant. The measurements were made above the threshold voltage and frequency. The phosphors whose EL-TL measurements are made were pre-excited for 10 minutes with an ultraviolet lamp (UV product, U.S.A. type UVS-12) emitting predominantly the 365 nm Hg doublet and were subsequently left decaying for fifteen minutes.

2.2.3 THERMOLUMINESCENCE MEASUREMENTS:

The experimental arrangement used and procedure followed for thermoluminescence measurements were same as that used for EL-TL measurements but without application of an electric field. Here also the samples were pre-excited for 10 minutes with ultraviolet lamp (UV products, U.S.A. type UVS-12) emitting predominantly the 365 nm Hg doublet and were subsequently left decaying for fifteen minutes. The heating rate used was 0.3°C/sec and TL measurements were carried out above room temperature within a range of 300°C to 415°C.
2.2.4 X-RAY DIFFRACTION MEASUREMENTS:

X-ray diffraction technique was employed to check the formation of solid solution of the prepared phosphors. X-ray spectrograms giving directly the intensity of diffracted beam were taken at the Regional Sophisticated Instrumentation Centre, I.I.T. Bombay. The X-ray diffractometer was operated at 31 kV, 20 mA using copper target and giving monochromatic X-ray wavelengths 1.54 Å (CuKα). The X-ray diffractometer has a Geiger counter for measuring the intensity of the diffracted beams for different values of 2θ. The scanning rate was 2°/min.

2.2.5 ELECTRON PARAMAGNETIC RESONANCE (EPR) MEASUREMENTS:

Electron paramagnetic resonance (EPR) spectra were recorded at the Regional Sophisticated Instrumentation Centre, I.I.T. Bombay. The EPR spectrometer used was an X-band Varian E-109 operated at a microwave frequency of 9.07 GHz and with 100 kHz field modulation. TCNE was used as a standard field marker taking gTCNE equal to 2.00399.

2.2.6 SCANNING ELECTRON MICROSCOPY STUDIES:

The SEM studies of the samples in the present investigation were carried out at Regional Sophisticated Instrumentation Centre, Nagpur. The electron microscope used was Cambridge Stereoscan 250 MK3. Phosphor pellets of appropriate size which can fit into the SEM chamber were prepared by applying pressure of 7 tones/cm² for five minutes. Prior to scanning, the samples were coated with a very thin metallic gold layer in order to minimize the charging effect or image blooming.
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<th>Sample NO.</th>
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REFERENCES


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Fig. 2.1. Experimental set up for electroluminescence
Fig. 2.2: Photograph of Experimental Set-up used in Electroluminescence Studies.
Fig. 2.3 - Circuit diagram of wide band amplifier
Fig. 2.4. (a) Electroluminescence cell
(b) Electro-thermoluminescence cell
FIG. 25. Spectral response curve for RCA931A PM tube.
Fig. 26. Experimental set up for electro-thermoluminescence